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ORIGINAL PAPER

Li-LiFePO$_4$ rechargeable polymer battery using dual composite polymer electrolytes

H. H. Sumathipala · J. Hassoun · S. Panero · B. Scrosati

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Abstracts A composite polymer electrolyte, formed by dispersing into a poly(ethylene oxide)-lithium salt matrix two additives, i.e. calyx(6)pyrrole, (CP) acting as an anion trapper and superacid zirconia, S-ZrO$_2$ acting as a conductivity promoter, has been tested as a separator in a new type of rechargeable lithium battery using lithium iron phosphate as the cathode. The choice of the electrolyte was motivated by its favourable transport properties both in terms of lithium ion transference number and of total ionic conductivity. The choice of the cathode was motivated by the value of its operating voltage which falls within the stability window of the electrolyte. The performance of the battery was determined by cycling tests carried out at various rates and at various temperatures. The results demonstrate the good rate capability of the battery which can operate at high charge-discharge efficiency even at 1 C rate and that it can be cycled at 90 °C with a satisfactory initial capacity of the order of 90 mAh g^{-1}. These values outline the practical relevance of the composite electrolyte membrane and of its use as separator in a lithium battery.

Keywords PEO-based composite polymer electrolyte · Lithium iron phosphate cathode · Lithium battery

1 Introduction

Lithium-ion batteries have attracted great attention due to their potential use in high-performance electric vehicles [1–3]. However, some problems still remain to be solved for the optimization of some critical operational features such as safety, design flexibility etc. Replacing of the conventional liquid electrolytes currently being used by a polymer membrane to form lithium polymer batteries is an effective approach for reaching this goal. In this scenario, PEO-LiX (X = CF$_3$SO$_3$, ClO$_4$, BF$_4$, BOB), membranes have been widely studied for practical applications [4–9].

However, these polymer electrolytes are still affected by some drawbacks, among which is the low lithium ion transference number which limits the power capability of the battery. We have recently introduced a new approach to improve the lithium ion transference number of PEO-based polymer electrolytes while still maintaining an overall high ionic conductivity [10]. These new electrolytes were formed by dispersing into a PEO-LiX matrix, e.g. a PEO-LiCF$_3$SO$_3$ matrix, two additives, i.e. calyx(6)Pyrrole, (CP) and superacid zirconia, S-ZrO$_2$. The CP macromolecule, due to the type of active groups in its lower rim, acts as expected as a very effective receptor of anions, thus greatly contributing to enhancement of the lithium transference number up to values close to unity. The superacid zirconia, due to specific interactions between the surface states and both the PEO chains and the lithium salts, enhances lithium ion transport and prevents formation of ionic couples, both effects contributing to enhancement of the overall conductivity of the polymer electrolyte [10].

In this work, a dual composite polymer electrolyte, i.e. PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$, was chosen as the electrolyte for the fabrication of a new type of lithium

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H. H. Sumathipala—On leave from Department of Physics University of Kelaniya, Kelaniya, Sri Lanka.

H. H. Sumathipala · J. Hassoun · S. Panero · B. Scrosati (✉)
Department of Chemistry, University of Rome, La Sapienza, 00185 Rome, Italy
e-mail: bruno.scrosati@uniroma1.it

rechargeable battery using lithium iron phosphate, $LiFePO_4$, as the preferred cathode.

The choice of electrolyte was motivated by the favorable results of our previous study which highlighted the practical relevance of the PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2 dual composite membrane in terms of lithium ion transference number, reported as high as 0.5, and of ionic conductivity, of the order of 10^{-4} S cm^{-1} [10]. The choice of cathode was motivated by its operating voltage which falls within the electrolyte stability limit [11].

2 Experimental

A hot pressed, solvent free PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2 composite membrane, previously discussed and characterized in our laboratory [10] was chosen as electrolyte. The battery was assembled by sandwiching a lithium metal foil anode, the selected polymer electrolyte membrane and a $LiFePO_4$-based composite cathode film. The latter was prepared by blending the $LiFePO_4$ active material (80%) with Super-P carbon as the electronic conducting additive (10 mass %) and PVdF 6020 Solvay Solef (10 mass %) as the binder. The battery was fabricated using an amount of cathode active mass in order that a cycling current of 0.22 A g^{-1} cm^{-2} should correspond to a rate of 1 C. The components of the cell were placed in a Teflon container with two stainless steel electrodes acting as current collectors. Care was taken to avoid direct contact between the metallic Li anode and the Teflon container. All assembly and test procedures were carried out in a controlled, argon atmosphere, drybox, having both humidity and oxygen content below 10 ppm.

The battery was characterised by galvanostatic cycling at temperatures varying from 80 °C to 100 °C and in a 3.0–3.8 V voltage range. The performance of the battery was evaluated in terms of specific capacity, charge/discharge efficiency and cycle life. Before the measurements the battery was kept at the highest testing temperature, i.e. at about 110 °C for at least 36 h to reach thermal equilibrium, as well as to allow lithium diffusion inside the cathode composite film. The operating temperatures of the battery were controlled by a Buchi oven and data acquisition was achieved using a Maccor 1400 battery tester.

3 Results and discussion

The charge-discharge process of the Li/PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/$LiFePO_4$ battery developed in this work is:

$$Li^+ + FePO_4 + e \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} LiFePO_4 \qquad (1)$$

to which is associated a maximum theoretical capacity of 170 mAh g^{-1} and a voltage plateau around 3.4 V Li/Li^+.

Figure 1 shows some typical voltage profiles of the lithium polymer battery cycled at 100 °C and at a C/0.8 rate. The voltage shows a near 3.4 V plateau expected on the basis of Eq. 1. The capacity, referred to the cathode, is of the order of 140 mAh g^{-1}, i.e. approaching 80% of the theoretical value.

Figure 2 shows a plot of specific capacity versus cycle number at different rates. Some interesting conclusions can be drawn from this result. First, there is a low initial charge-discharge efficiency, due to various phenomena, such as (i) decomposition of the electrolyte with the formation of a passivating layer on the anode surface [12], and (ii) the formation of a barrier potential due to anion accumulation in the vicinity of the anode-electrolyte interface hindering lithium ion motion during the subsequent discharge [13]. The latter phenomenon may take place whenever the C-rate changes: the larger the C-rate, the larger the barrier potential and vice versa. Identification of the causes of the initial capacity decay, however, remains to be established and work is in progress to fully clarify them.

Figure 2 also shows the good rate capability of the battery which can operate at high charge-discharge efficiency over all the tested rates. This is further confirmed by Fig. 3 which shows the trend of the specific capacity versus current density and versus the reciprocal of cycling rate. The capacity declines linearly up to a current density of 0.15 mA cm^{-2} to then abruptly decay. Thus, 0.15 mA cm^{-2}

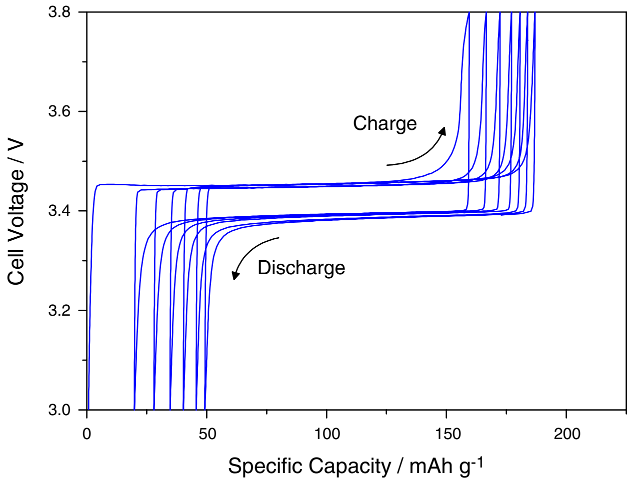

Fig. 1 Typical voltage vs. specific capacity profiles of some consecutive cycles at 100 °C of the Li/PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/Li_4FePO_4 polymer battery at C/8 rate, corresponding to a current density of 0.075 mA cm^{-2}

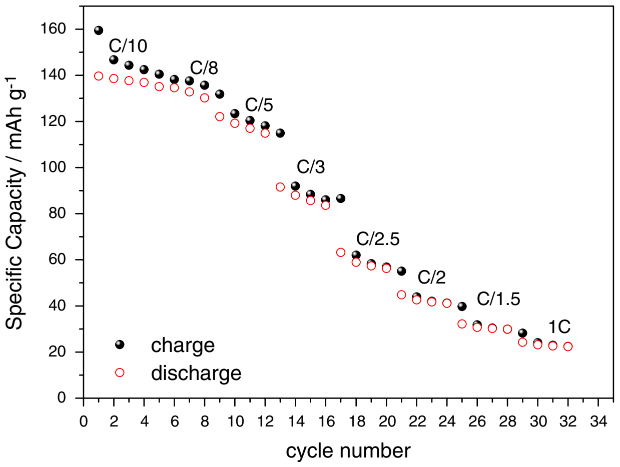

Fig. 2 Capacity versus cycle number of the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ polymer battery at 100 °C and at various rates

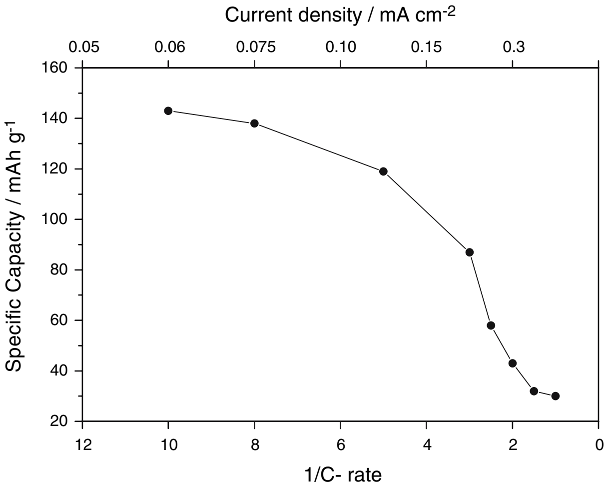

Fig. 3 Specific capacity vs. current density and the reciprocal 1/C rate for the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ polymer battery at 108 °C

may be assumed as the limiting current density. This value is higher than that previously obtained for conventional Li polymers batteries, reported to be of the order of 0.1 mA cm^{-2} [14, 15]. The high value of the limiting diffusion current density found for the present battery is associated with the high lithium ion transference number of the selected polymer electrolytes [10].

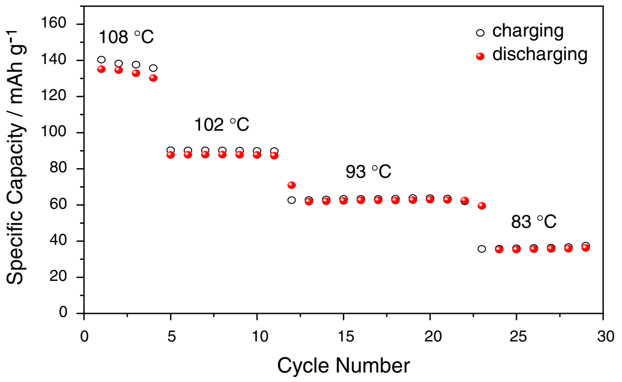

Fig. 4 Specific capacity vs. cycle number for the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ polymer battery at various temperatures and at a C/8 rate

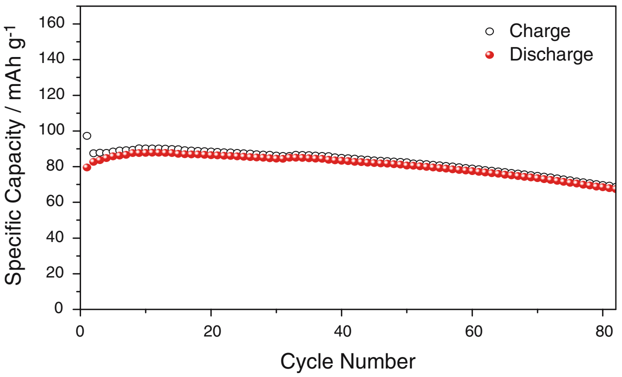

Fig. 5 Cycling performance of the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ polymer battery at 102 °C and at C/8 rate (Current density: 0.075 mA cm^{-2})

The response of the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ battery was also studied at various temperatures. Accordingly, the battery was cycled at 108 °C at the C/8 rate, then the temperature was lowered and maintained at the new value for several hours to reach the thermal equilibrium before the test restarted. Figure 4, which summarizes the charge/discharge results, shows that the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ battery can be cycled with a satisfactory value of capacity only when the temperature is higher than 93 °C. The capacity decay at lower temperature may be attributed to various factors, the main being the decline in the ionic conductivity of the polymer electrolyte. There are promising indications, however, of further improvement in the battery performance for low power applications.

Figure 5 shows the cycling performance of the Li/PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$/Li$_4$FePO$_4$ battery under the best operating conditions, i.e., at ~100 °C and at C/8 rate. A charge/discharge efficiency approaching 100% and a capacity of the order of 90 mAh g^{-1} were obtained. These values are of interest and confirm the practical importance of the dual-composite polymer electrolyte for battery application, although further research is needed to optimize the cell structure and improve the membrane properties.

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